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Speciation of trace metals in relation to degradation of organic matter in marine sediment slurries

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SUMMARY

In this study continuously stirred sediment slurries were used. The slurry incubations were performed at constant pH (7.8), temperatures (14 and 4°C), salinity (25‰) and at different, well defined O₂ concentrations (100%, 20% and 0% air saturation). The dissolved metal concentrations of Cu, Cd, Ni, Pb, Fe and Mn were recorded as a function of time. In order to relate changes in dissolved metal concentrations with degradation of organic matter, these degradation rates were estimated by means of several parameters like O₂, DOC concentration and nutrients. Sequential extractions of metals from the sediment were used to indicate changes in availability of metals in the sediment as a result of degradation of organic matter and to compare this availability at different O₂ concentrations.

Chapter 1

In Chapter 1 an experiment under aerobic conditions (100% air saturation) is described. The dissolved and particulate organic matter (DOM and POM) were oxidized during the experiment. Oxygen consumption was high in the beginning of the experiment during the degradation of DOM, after which it decreased to a constant value. The degradation of POM was reflected by an increase of inorganic N (inorg. N).

Dissolved Cu and Ni were positively related with DOC in the beginning of the experiment, indicating complexation of these metals with dissolved organic ligands. After the decrease in DOC, Cu and Cd were positively related with the increase of inorg. N. Thus, these metals were released during the degradation of POM.

Results of the sequential extractions of the sediment showed an increase in time of the easily extractable fractions for Cu, Cd, Pb and Zn, which indicated that these metals became more mobile under the prevailing conditions. Mn became more difficult to extract and the extractability of Ni did not change in time.

Chapter 2

In Chapter 2 incubations at 20% air saturation and under anaerobic conditions are treated.

At 20% air saturation the degradation of POM occurred simultaneously with O₂ reduction, nitrate reduction and reduction of solid Fe(hydr)oxides. DOM degraded at a slower rate than under aerobic conditions. Cu showed a reduced tendency to form complexes with dissolved organic ligands compared to during the experiment under aerobic conditions. Dissolved Ni on the other hand showed the same relation with DOC as under aerobic conditions.

At 0% air saturation the degradation of POM occurred simultaneously with

Fe(hydr)oxides reduction and sulphate reduction. Comparison with the release of dissolved Fe at 20% air saturation proved that the Fe(hydr)oxides were only partly reduced at this air saturation level. Degradation of DOM was even slower than at 20% air saturation. Thus, oxygen is very important for degradation of DOM. The degradation of POM however, occurred at least at the same rate and perhaps even faster than under aerobic conditions (100% air saturation).

Cu and Cd could not be detected in the dissolved phase, probably due to sulfide formation. The dissolved Ni concentration was low compared to its concentration at 20% and 100% air saturation. Cu, Cd, Pb and Zn were more difficult to extract from the sediment compared to during the experiment under aerobic conditions. Speciation of Ni in the sediment was not influenced by the lack of oxygen. Upon introduction of air these above mentioned four metals became easier to extract within six days. In contrast to its almost inert behaviour in the sediment, Ni was readily mobilized (within one day) to form dissolved organic complexes to an extent comparable to during the experiment under aerobic conditions. The release of Cu from the sediment, to form dissolved organic complexes, was slower. It took at least two days before Cu reached dissolved concentrations comparable to those during the aerobic experiment. As well in solution as in the sediment the kinetics of Fe reduction and Mn oxidation were relatively slow (8 days and more than 3 days respectively), whereas Fe oxidation and Mn reduction were relatively fast (within 12 hours and within 1 day respectively).

Chapter 3

The correlations between Cu and DOC under aerobic conditions (100% air saturation) and between Ni and DOC under aerobic conditions and at 20% air saturation, proved the importance of dissolved organic ligands for the speciation of these metals. Moreover it seemed that in the beginning of the aerobic experiment the release of these metals from the sediment and thus their total dissolved concentrations were governed by the concentration of dissolved organic ligands.

In Chapter 3 the determination of the organic ligand concentrations and the conditional stability constants of the metal organic complexes are discussed.

Two groups of organic ligands could be distinguished, a relatively polar and a relatively hydrophobic ligand group. The conditional stability constant of the Cu polar ligand complex was found to be $10^{11.1}$, that of the Cu hydrophobic ligand complex $10^{8.7}$, in line with other observations (Coale and Bruland, 1988; Sunda and Hanson, 1987). Within 2-3 days the relatively polar ligand sites became saturated with Cu. The concentration of the relatively polar ligand decreased in time due to the oxidation of dissolved

organic matter; that of the more hydrophobic ligand seemed to remain constant. The free Cu concentration increased considerably in time. This increase in free Cu was due to the lower stability constant of the relatively hydrophobic complex, which governed the free Cu concentration after the saturation of the relatively polar ligand sites.

The conditional stability constant of the Ni polar ligand complex was difficult to obtain because the ligand sites were saturated with Ni; probably it was around 10^{10} . It was not sure whether Ni was reversibly complexed with this ligand. The relatively polar ligand concentration decreased linearly in time together with the decrease of DOC. After 31 days these ligands were totally oxidized. The conditional stability constant of the Ni-hydrophobic ligand complex was found to be $10^{8.5}$. The concentration of the relatively hydrophobic ligands remained constant in time, suggesting that the organic matter is of a refractory nature.

Chapter 4

Cu was obviously associated with DOM and POM under aerobic conditions. The results from the sequential extraction procedure (Chapter 1) showed an increasing association of Cu with a certain type of organic matter in time. The extraction step in question extracts, amongst others, low molecular weight humic and fulvic acids. Therefore the question came up whether coinciding changes could be detected in the character of POM and in the amounts of its different fractions.

In Chapter 4 fulvic acids (FA), humic acids (HA) and an acid-extractable fraction were extracted from sediment samples taken during an aerobic slurry experiment. From the same samples Cu was extracted according to the sequential extraction procedure. FA's and HA's were characterized by IR spectroscopy and UV absorption measurements.

Changes with time in the characteristics of POM and in the amounts of the different fractions were small. The different results however pointed in the same direction. The amount of FA's increased linearly with time, while the molecular size of the FA's and HA's probably decreased with time. The increase of FA's and the decrease in molecular size of FA's and HA's resulted both in increasing complexation capacities of the organic acids with regard to Cu. This coincides well with the results of the sequential extraction for Cu. Moreover the results indicated that, during the degradation of organic matter, FA's were formed out of HA's according to the so-called degradative pathway theory (Hatcher and Spiker, 1988).

Resuming, it can be said that under strict aerobic conditions (100% air saturation) the concentration of dissolved organic ligands determines the concentrations of dissolved Cu and Ni in the water phase of the slurry. Degradation of the strongest of the two organic ligand groups results in

higher free Cu concentrations and thus higher Cu toxicity.

During the degradation of POM, Cu and Cd in the sediment become more easy to extract. The larger availability of Cu in the sediment is reflected by a faster release, with respect to the start of the experiment, upon the addition of dissolved organic ligands. The increase of fulvic acids in the sediment with time and the association of Cu with these new fulvic acids can explain the increase in availability of Cu in the sediment.

The release of Cd to the waterphase in the slurry experiments seems to be directly related to the degradation of POM.

At the natural sediment-water interface an increase of dissolved organic ligands by an algal bloom or by pollution should induce a flux of Cu and Ni from the aerated top-layer of the sediment to the overlying water within 15 minutes (at 14°C).

As well at 20% air saturation as under anaerobic conditions (0% air saturation), the dissolved Cu and Cd concentrations are below the detection limit of our method (respectively 2 and 0.1 nanomol/l). However, a decrease from 100% to 20% air saturation does not result in a decrease of the dissolved Ni concentration. At 20% air saturation Ni probably exists as a dissolved organic complex. Only under anaerobic conditions a decrease in the dissolved Ni concentration was observed.

The results from the slurry incubations confirm the fact that sampling of pore waters of coastal sediments for the analysis of trace metals should be preceded by measuring the O₂-profile in the sediment. Only then, mixing of pore waters with large differences of metal concentrations can be prevented.

The introduction of air in the anaerobic slurry experiment results in an immediate (within 1 hour) release of Ni into the dissolved phase, followed within three days by Cu. The dissolution of Cd starts only after 6 days. The availability of Cu, Cd, Pb and Zn in the sediment increased within 6 days to that as during the aerobic experiment.

In coastal sediments the oxygen penetration depth varies due to changes in current velocity of the overlying water, erosion and deposition of sediment and by inputs of organic matter. According to the results of the slurry experiments, changes in oxygen concentration in the sediment should influence the dissolved concentration of Ni immediately and, depending on the duration of the change, also those of Cu and Cd.